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(71) Applicant *(for all designated States except US)*: **SKYRAD LTD.** [IL/IL]; Gutwirin Science Park, Technion, 32000 Haifa (IL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **FARAN, Ori** [IL/IL]; Beilis Street 4/6, 34814 Haifa (IL). **NATAN, Ezra** [IL/IL]; Alexander Yannay Street 46/2, 34816 Haifa (IL).

(74) Agent: **AGRANOV, David**; Moriah Ave. 20, 34571 Haifa (IL).

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(54) Title: THERMOCHROMIC COMPOSITION

(57) Abstract: A novel reversible thermochromic composition comprising (1) a main organic component, capable to change its color upon applying thermal energy thereto and (2) an auxiliary organic component, rendering said main organic component the capability to change its color at predetermined temperature. Both components are incorporated within a polymer matrix. The articles made of this composition change their color or became colorless at predetermined temperature and they have accurate temperature response. The manufacturing process is simple, inexpensive and can be carried out by conventional technology routes.

Thermochromic composition

Abstract

A novel reversible thermochromic composition comprising (1) a main organic component, capable to change its color upon applying thermal energy thereto and (2) an auxiliary organic component, rendering said main organic component the capability to change its color at predetermined temperature. Both components are incorporated within a polymer matrix. The articles made of this composition change their color or became colorless at predetermined temperature and they have accurate temperature response.

The manufacturing process is simple, inexpensive and can be carried out by conventional technology routes.

Field of the invention

The present invention refers to organic compositions, exhibiting the known phenomena named thermochromism, which is thermally induced reversible transformation of a molecular structure of the composition, accompanied by a spectral change, typically of visible color.

Background of the invention

There are known compositions or substances, which exhibit thermochromism, e.g. when, heated to a certain temperature change their color or became colorless. These materials can be divided into three categories:

A. Inorganic compounds, which comprise double salts of a transition metal (Co,Ni,Mg) and of an aminic amide and simple salts like mercury iodide and lead chromate. The main disadvantages of these materials are:
    1. High toxicity.
    2. Limited choice of colors, appearing by temperature change
    3. Limited choice of transition temperatures, at which the color changes

4. Insufficient intensity of color, accompanying the change of temperature.

B. Organic substances, also known as dyes that are intrinsically thermochromic and which exhibit change of color either upon exposure to infrared radiation (see US 5426143). The main disadvantage of this group is associated with the necessity to apply relatively high temperature for inducing thermochromic effect. Besides all the limitations except of toxicity, mentioned in connection with the item A are also exist. It can be readily appreciated that all above limitations restrict the field of possible applications.

C. Organic compositions, employing so-called electron-donating chromogenic material and an electron-accepting color developer. These thermochromic compositions need at least three different components, (1) an electron-donating chromogenic material, (2) an electron accepting color developer, (3) a solvent e.g. alcohol, an amide or an ester. Examples of these compositions are described in US patents no. 4717710, 4957949, 5431697, and 6048387. Their disadvantages are:

1. The necessary in using of at least three different components.
2. The manufacturing process of these compositions is long and complicate and therefore their final cost is high, which limits their use in commercial products.
3. The concentration of these compositions in polymeric matrix should be relatively high (2-40%), and this may deteriorate the physical properties of the polymer.
4. Their temperature response is insufficiently accurate, since the temperature interval in which the thermochromic effect takes place is relatively large (about $10^{O}C$).

The above disadvantages limit the commercial use of available thermochromic materials to a narrow range of products, mainly toys.

Therefore despite of existence of certain thermochromic compositions and articles made therefrom there still is felt a strong need in a novel thermochromic composition,

which is convenient in use and manufacturing, is inexpensive, and which has thermal response in narrow range of temperatures.

Summary of the invention

The present novel invention intends to provide a new and improved reversible thermochromic composition that is capable either to get colored by a high intensity color or to get absolutely discolored at a predetermined temperature.

After comprehensive studies of a thermochromic color-developing system based on a chromogenic organic component and an auxiliary stabilizing organic component, it was empirically revealed by the inventors of the present invention that the above requirements are satisfied by virtue of a mixture comprising solely these two components homogeneously incorporated within a host medium. Furthermore, it was discovered that by varying of the chromogenic organic component and the auxiliary organic component it is possible to achieve large variety of color. It was also found, that certain amount by % weight of each component and the different proportions between these two components cause a reversible change of color at a specified temperature. It was also found, that by changing the proportions between these two components in the composition, it is possible to control the number of coloration-discoloration cycles and that after certain time and at certain temperature the coloration thermochromic effect becomes irreversible and so the color of an article made of such composition.

Within the range of possible applications for the new composition are for example industrial safety applications:

a) electrical, (plugs, sockets, contactors)

b) mechanical (ventilation openings, covers)

c) chemical (containers for toxic wastes, packages etc.)..

By addition of the composition of the invention to the above electrical appliances or mechanical parts one can quickly visually detect their failure, due to the color change caused by heating.

In the chemical safety area the change of color gives early warning about possible failure due to initiation of the chemical reaction.

Other safety applications include safety products for children (warm bottle), agriculture (temperature sensors), medicine and food (containers).

Other application are time temperature indicators (TTI), which are used in chilling or frosting of food products, storing drugs and chemicals to indicate deviation from the required storage condition.

List of drawings

Figs.1-4 are general structural formulae of various organic compounds suitable for use in the composition of the present invention

Detailed description of the preferred embodiments

The thermochromic composition of the present invention is a mixture of two components , which are:

1) A main organic component, exhibiting chromogenic properties and
2) An auxiliary organic component, capable to stabilize the structure of the main organic component.

In the further description the main organic component will be referred to as chromogenic component and the auxiliary component will be referred to as stabilizing component.

Non limiting examples of organic compounds, suitable for use as chromogenic component comprise:

1) Spirobenzopyrans derivatives, having general formula A, shown in Fig.1.

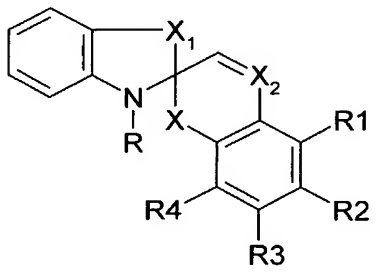


Fig.1, Formula A

In the above formula X = O or S; X_1 = O, S or CR'R'' where R' and R'' are independently a hydrogen, an alkyl group a halogen or only a sole group, like a substituted alkyl ring; X_2 = N or CH; and R, R_1, R_2, R_3, R_4, represent independently a hydrogen, an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. R_1-R_2, R_2-R_3, R_3-R_4 can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group.

2) Spiropyranopyrans derivatives, having general formula B, shown in Fig.2.

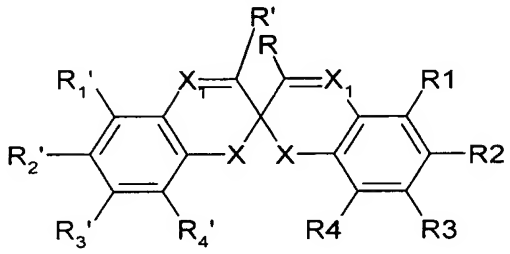


Fig.2, Formula B

In the above formula X = O or S; X_1 = N or CR_5; and R, R_1, R_2, R_3, R_4, R_5, R', R_1', R_2', R_3', R_4' represent independently a hydrogen, an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. R_1-R_2, R_2-R_3, R_3-R_4, R_1'-R_2', R_2'-R_3', R_3'-R_4'can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group.

3) Spiroquinolinopyrans derivatives, having general formula C, shown in Fig.3.

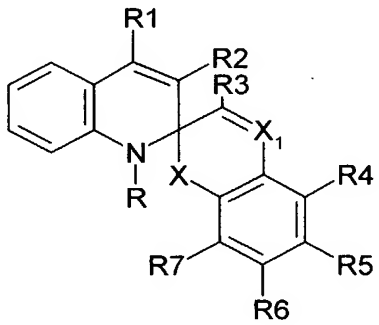
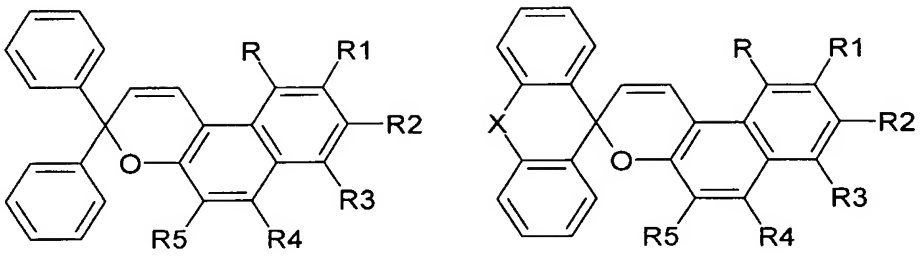


Fig.3, Formula C

In the above formula X=O or S; X_1=N or CR'; and R', R, R_1, R_2, R_3, R_4, R_5, R_6, R_7 represent independently a hydrogen, an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. R_4-R_5, R_5-R_6, R_6-R_7 can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group.

4) Naphthopyrans derivatives, having general formula D, shown in Fig.4.



D E

Fig.4, Formulae D, E

In the above formula X=O, S, N-R' with R' an alkyl group or a functionalized group, $(CH_2)_n$ and n= 0, 1. R, R_1, R_2, R_3, R_4, R_5 represent independently a hydrogen an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. R-R_1, R_1-R_2, R_2-R_3, R_4-R_5 can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group.

Each of the above organic compounds can be used in the composition being taken alone or in combination with the other compounds. The amount of the chromogenic component in the composition of the invention lies between 0.005% and 0.5% by weight of the total composition.

Non-limiting examples of organic compounds, capable to stabilize the structure of the chromogenic component and suitable for use as auxiliary component comprise:

- Benzylidene-1,1'-di-2-naphthol
- 2-hydroxybenzylidene-1,1'-di-2-naphthol
- 3-hydroxybenzylidene-1,1'-di-2-naphthol
- 3-aminobenzylidene-1,1'-di-2-naphthol
- 3-nitrobenzylidene-1,1'-di-2-naphthol
- 3-hydroxybenzylidene-1,1'-di-2-naphthol
- 2-hydroxy-3-aminobenzylidene-1,1'-di-2-naphthol
- 2-hydroxy-3-nitrobenzylidene-1,1'-di-2-naphthol
- 2-hydroxy-3-methoxybenzylidene-1,1'-di-2-naphthol
- 2-chloro-5-nitrobenzylidene-1,1'-di-2-naphthol
- 2-chloro-5-aminobenzylidene-1,1'-di-2-naphthol
- 3-amino-4-hydroxy-5- methoxybenzylidene-1,1'-di-2-naphthol

- 4,4'isopropylidenediphenol
- 4,4'isopropylidenebis(2,6-dimethyl-phenol)
- 4,4'ethylidenebisphenol
- Bis(4-hydroxyphenyl)methane
- Bis(4-glycidyloxyphenyl)methane
- 4,4'(1,3-phenylenediisopropylidene)bisphenol
- 4,4'-sulfonyldiphenol
- 4,4'cyclohexylidenebisphenol
- 4,4'isopropylidenediphenol
- 4,4'isopropylidenebis(2,6-dimethyl-phenol)
- 4,4'ethylidenebisphenol
- Bis(4-hydroxyphenyl)methane
- Bis(4-glycidyloxyphenyl)methane
- 4,4'(1,3-phenylenediisopropylidene)bisphenol
- 4,4'-sulfonyldiphenol
- 4,4'cyclohexylidenebisphenol
- α, α'-di(2-hydroxy-1-naphthyl)-p-tolyl-benzoic acid ester
- (α, α'-di(2-hydroxy-1-naphthyl)-o-tolyl)-sulphonic acid ester of 6-diazo-5,6dihydro-5-oxo-1-naphtalene
- (3-methoxy-α, α'-di(2-hydroxy-1-naphthyl)-p-tolyl)-sulphonic acid ester of 6-diazo-5,6dihydro-5-oxo-1-naphtalene
- {α-[2-(2-diazo-1,2- dihydro-1-oxo-5- naphthyl-sulphonyloxy)-1- naphthyl]- α- (2-hydroxy-1- naphthyl)-o-tolyl} sulphonic acid ester of 6-diazo-5,6dihydro-5-oxo-1-naphtalene
- Bis(2-methyl-3-indolyl)-methyl-p-anisol

Each of the above organic compounds can be used in the composition as stabilizing component being taken alone or in combination with the other compounds. The amount of the stabilizing component in the composition of the invention lies between 0.005% and 2% by weight of the total composition.

It has been unexpectedly revealed that the composition containing the above components, exhibits thermochromic effect at a certain temperature within a wide

range of temperatures from -10°C up to 110 °C. The change of the color is remarkable, since the new color has strong intensity. Furthermore, it was discovered, that the thermochromic effect is reversible and repeatable, in the sense, that the composition can be returned to the initial color and then again to the new color by proper changing of the temperature.

In practice, the thermochromic composition is incorporated within a polymeric matrix. Non-limiting examples of suitable polymeric matrices comprise various optically transparent or semi opaque plastic materials, e.g. polycarbonates, polystyrenes, polyolefins, polyacrylates such as polymethylmethacrylates, polyvinyl derivatives, polyesther derivatives, polyvinyl chloride; cellulose derivatives such as cellulose acetate, polyurethanes, polyethylene terephthalate; silicone resins such as LSR (liquid silicone rubber), triethylene glycole dimethacrylate (TEGDM, commercially known as CR-39), epoxy resins. Transparent copolymers and blends of dissimilar transparent polymers are also suitable as host material.

It might advantageous if the composition includes also at least one functional additive, like plastisizers, e.g. phtalic acid esters, phosphoric esters, adipic acid derivatives, camphor, etc, taken alone or in any combination.

The preferred methods of manufacturing of an article from the composition of the invention are injection molding (including co-injection in the case of more complicated articles), extruding (including co-extruding), blow molding.

When required, the matrix may include further functional additives, such as dyes, pigments, ultraviolet absorbers etc. Among such possible additives are 2-hydroxy-4-(N-octoxy)benzophenone, 2-(2-hydroxy-5-methyl-phenyl)-2H-benzotriazole, 2-(2H-benzotriazol-2-YL)-4,6-ditertpentylphenol and the like, metal powders, antioxidants, reduction preventing agents, reducing agents, chelating agents, flame retardant, etc.

The total amount of additives lies between 0 and 2% by weight of the total composition.

The present invention will be now described in details with reference to the following non-limiting examples. The examples refer to compositions and manufacturing of articles, made of the compositions.

Example 1:

An article was prepared from a chromogenic organic component namely 1',3'-dihydro-1'benzyl-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indoline],having the formula A shown in Fig 1. The composition contained also a stabilizing component, namely 2-hydroxy-3-nitrobenzylidene-1,1'-di-2-naphthol and a functional additive, namely UV absorber Tinuvin P, manufactured by Ciba Geigy Ltd, Switzerland.

The components were added to low-density polyethylene by compounding at 200°C, with subsequent injection molding to obtain desired form of the article.

The amounts of the components in the composition were as follows:

Chromogenic component	0.02% by weight
Stabilizing component	0.005% by weight
Functional additive	0.2% by weight
Polymeric matrix	Rest

The article was colorless at room temperature, and became magenta colored at -10°C. This process of discoloration-coloration was repeated many times without significant change of the intensity of the color.

Example 2:

An article was prepared from a composition, including chromogenic organic component namely 1',3'-dihydro-1'butyl-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indoline], having the formula A shown in Fig 1. The composition contained also a stabilizing component, namely 2-hydroxy-3-nitrobenzylidene-1,1'-di-2-naphthol. The components were added to low-density polyethylene by compounding at 200°C with subsequent injection molding to obtain desired form of the article.

The amounts of the components in the composition were as follows:

Chromogenic component	0.02% by weight
Stabilizing component	0.03% by weight
Polymeric matrix	Rest

The article color was magenta colored at room temperature and became transparent at 60°C without any residual color. This process of discoloration-coloration was repeated many times without significant change of the initial magenta color.

The article was subjected to temperature of 60°C for 30 hours after which it became irreversibly transparent at any temperature.

Example 3:

An article was prepared from a composition including a chromogenic organic component namely 1',3'-dihydro-1'benzyl-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indoline], having the formula shown A in Fig 1. The composition contained also stabilizing organic component agent namely 2-hydroxy-3-nitrobenzylidene-1,1'-di-2-naphthol. These materials were added to low-density polyethylene by compounding at 200°C, with subsequent injection molding to obtain desired form of the article.

The amounts of the components in the composition were as follows:

Chromogenic component	0.05% by weight
Stabilizing component	0.013% by weight
Polymeric matrix	Rest

The article color was magenta colored at room temperature, and became transparent at 110°C and this without any residual colors. This process of discoloration-coloration was repeated many times without significant change of the initially colored article.

The article was subjected to temperature of 110°C for 100 hours after which it became irreversibly transparent at any temperature.

Example 4:

An article was prepared from a composition, including a chromogenic organic component namely 1',3'-dihydro-1'benzyl-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indoline], having the formula A shown in Fig 1. The composition contained also stabilizing organic component, namely 2-hydroxy-3-nitrobenzylidene-1,1'-di-2-naphthol and functional additive, namely yellow pigment 022310, manufactured by Tosaf Ltd, Israel. The components were added to low-density polyethylene by compounding at 200°C, with subsequent injection molding to obtain desired form of the article.

The amounts of the components in the composition were as follows:

Chromogenic component	0.025% by weight
Stabilizing component	0.062% by weight
Functional additive	0.1% by weight
Polymeric matrix	Rest

The article color was magenta colored at room temperature, and became yellow at 85°C. This process of discoloration-coloration was repeated many times without significant change of the initial color.

Example 5:

An article was prepared from a composition, containing a chromogenic organic component namely 1',3'-dihydro-1'benzyl-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indoline], having the formula A shown in Fig 1. The composition contained also stabilizing organic agent namely 2-hydroxy-3-nitrobenzylidene-1,1'-di-2-naphthol and functional additives, namely red pigment L5418 manufactured by Kafrit Ltd, Israel and flame retardant agent namely Deca-bromodiphenyl oxide manufactured by Bromine Ltd. Israel. The components were added to low-density polyethylene by compounding at 200°C, with subsequent injection molding to obtain desired form of the article.

The amounts of the components in the composition were as follows:

Chromogenic component	0.052% by weight
Stabilizing component	0.062% by weight
Red pigment	0.03% by weight
Flame retardation agent	1% by weight
Polymeric matrix	Rest

The article color was magenta colored at room temperature, and became red at 85°C. This process of discoloration-coloration was repeated many times without significant change of the initial color.

Example 6:

An article was prepared from a composition, containing a chromogenic organic component namely 1',3'-dihydro-1'butyl-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indoline], having the formula A shown in Fig 1. The composition also contained stabilizing organic agent namely 2-hydroxy-3-nitrobenzylidene-1,1'-di-2-naphthol and functional additives, namely red pigment L5418 manufactured by Kafrit Ltd, Israel and antioxidant agent Irganox 1010 manufactured by Ciba Geigy Ltd, Switzerland. The components were added to the low-density polyethylene by compounding at 200°C, with subsequent injection molding to obtain desired form of the article.

The amounts of the components in the composition were as follows:

Chromogenic component	0.025% by weight
Stabilizing component	0.062% by weight
Red pigment	0.03% by weight
Antioxidant agent	0.2% by weight
Polymeric matrix	Rest

The article color was magenta colored at room temperature, and became red at 85°C. This process of discoloration-coloration was repeated many times without significant change of the initial color.

Example 7:

An article was prepared from a composition including a chromogenic organic component namely 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3'-(3H)phenanthr[9,10-*b*][1,4]oxazine], having the formula shown C in Fig 3. The composition contained also stabilizing organic component agent namely 4,4'-sulfonyldiphenol and functional additives, namely red pigment L5418 manufactured by Kafrit Ltd. These materials were added to low-density polyethylene by compounding at 200°C, with subsequent injection molding to obtain desired form of the article.

The amounts of the components in the composition were as follows:

Chromogenic component	0.05% by weight
Stabilizing component	0.15% by weight
Red pigment	0.03% by weight
Polymeric matrix	Rest

The article color was blue colored at room temperature, and became red at 120°C and this without any residual colors. This process of discoloration-coloration was repeated many times without significant change of the initially colored article.

Example 8:

An article was prepared from a composition including a chromogenic organic component namely diphenyl-3*H*-naphthopyran[2,1-b]pyran, having the formula D shown in Fig 4. The composition contained also stabilizing organic component agent namely 4,4'-sulfonyldiphenol. These materials were added to low-density polyethylene by compounding at 200°C, with subsequent injection molding to obtain desired form of the article.

The amounts of the components in the composition were as follows:

Chromogenic component	0.05% by weight
Stabilizing component	0.1% by weight
Polymeric matrix	Rest

The article color was yellow-orange colored at room temperature, and became transparent at 130°C and this without any residual colors. This process of discoloration-coloration was repeated many times without significant change of the initially colored article.

It should be appreciated that the present invention is not limited by the above-described embodiments and that one ordinarily skilled in the art can make changes and modifications without deviation from the scope of the invention as will be defined below in the appended claims.

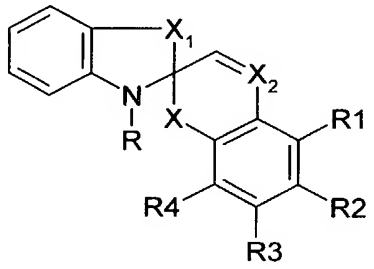
Claims

We claim:

1. A thermochromic composition comprising
   a) at least one chromogenic organic component, capable to change the color of the composition or discolorate thereof upon applying thermal energy,
   b) at least one stabilizing organic component, capable to render the change of color or discoloration visually detectable.

2. The thermochromic composition as defined in claim 1, in which said chromogenic organic component is selected from the group comprising:

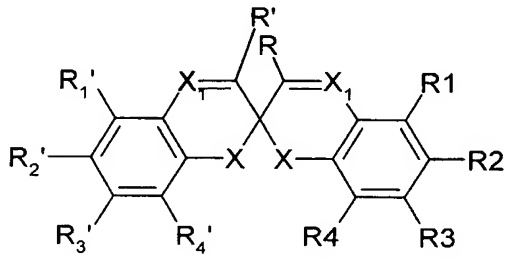
a) Spirobenzopyrans derivatives, having general formula A



A

in the above formula X = O or S; X_1 = O, S or CR'R'' where R' and R'' are independently a hydrogen, an alkyl group a halogen or only a sole group, like a substituted alkyl ring; X_2 = N or CH; and R, R_1, R_2, R_3, R_4, represent independently a hydrogen, an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. R_1-R_2, R_2-R_3, R_3-R_4 can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group,

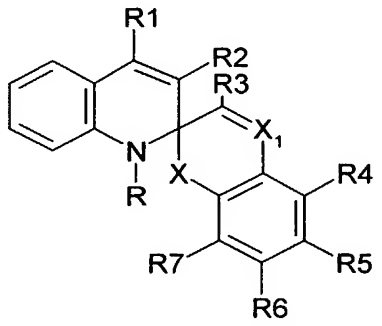
b) Spiropyranopyrans derivatives, having general formula B



B

in the above formula X = O or S; X_1 = N or CR_5; and R, R_1, R_2, R_3, R_4, R_5, R', R_1', R_2', R_3', R_4' represent independently a hydrogen, an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. R_1-R_2, R_2-R_3, R_3-R_4, R_1'-R_2', R_2'-R_3', R_3'-R_4'can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group,

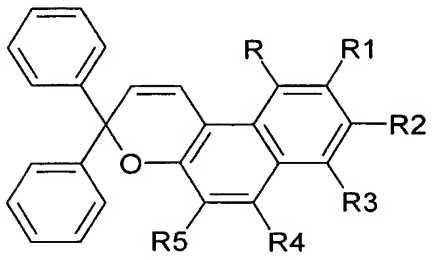
c) Spiroquinolinopyrans derivatives, having general formula C,



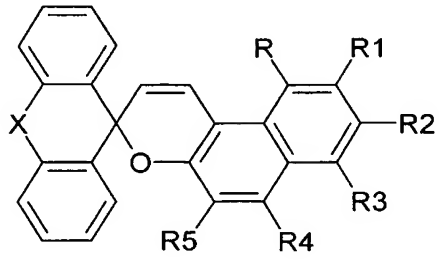
C

in the above formula X=O or S; X_1=N or CR'; and R', R, R_1, R_2, R_3, R_4, R_5, R_6, R_7 represent independently a hydrogen, an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. R_4-R_5, R_5-R_6, R_6-R_7 can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group,

d) Naphthopyrans derivatives, having general formula D or E



D



E

in the above formulae X=O, S, N-R' with R' an alkyl group or a functionalized group, $(CH_2)_n$ and n= 0, 1. R, R_1, R_2, R_3, R_4, R_5 represent independently a hydrogen an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. R-R_1, R_1-R_2, R_2-R_3, R_4-R_5 can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group,

and said stabilizing organic component is selected from the group comprising

- Benzylidene-1,1'-di-2-naphthol
- 2-hydroxybenzylidene-1,1'-di-2-naphthol
- 3-hydroxybenzylidene-1,1'-di-2-naphthol
- 3-aminobenzylidene-1,1'-di-2-naphthol
- 3-nitrobenzylidene-1,1'-di-2-naphthol
- 3-hydroxybenzylidene-1,1'-di-2-naphthol
- 2-hydroxy-3-aminobenzylidene-1,1'-di-2-naphthol
- 2-hydroxy-3-nitrobenzylidene-1,1'-di-2-naphthol
- 2-hydroxy-3-methoxybenzylidene-1,1'-di-2-naphthol
- 2-chloro-5-nitrobenzylidene-1,1'-di-2-naphthol
- 2-chloro-5-aminobenzylidene-1,1'-di-2-naphthol
- 3-amino-4-hydroxy-5- methoxybenzylidene-1,1'-di-2-naphthol
- 4,4'isopropylidenediphenol
- 4,4'isopropylidenebis(2,6-dimethyl-phenol).
- 4,4'ethylidenebisphenol
- Bis(4-hydroxyphenyl)methane
- Bis(4-glycidyloxyphenyl)methane
- 4,4'(1,3-phenylenediisopropylidene)bisphenol
- 4,4'-sulfonyldiphenol
- 4,4'cyclohexylidenebisphenol
- 4,4'isopropylidenediphenol
- 4,4'isopropylidenebis(2,6-dimethyl-phenol)
- 4,4'ethylidenebisphenol
- Bis(4-hydroxyphenyl)methane
- Bis(4-glycidyloxyphenyl)methane
- 4,4'(1,3-phenylenediisopropylidene)bisphenol

- 4,4'-sulfonyldiphenol
- 4,4'cyclohexylidenebisphenol
- α, α'-di(2-hydroxy-1-naphthyl)-p-tolyl-benzoic acid ester
- (α, α'-di(2-hydroxy-1-naphthyl)-o-tolyl)-sulphonic acid ester of 6-diazo-5,6dihydro- 5-oxo-1-naphtalene
- (3-methoxy-α, α'-di(2-hydroxy-1-naphthyl)-p-tolyl)-sulphonic acid ester of 6-diazo-5,6dihydro-5-oxo-1-naphtalene
- {α-[2-(2-diazo-1,2- dihydro-1-oxo-5- naphthyl-sulphonyloxy)-1- naphthyl]-α- (2-hydroxy-1- naphthyl)-o-tolyl} sulphonic acid ester of 6-diazo-5,6dihydro-5-oxo-1-naphtalene
- Bis(2-methyl-3-indolyl)-methyl-p-anisol

3. The thermochromic composition as defined in claim 1, in which said chromogenic component and said stabilizing component are incorporated within a polymeric matrix.

4. The thermochromic composition as defined in claim 3, said composition containing 0.005-0.5 % by weight of the chromogenic component, 0.05-2% by weight of the stabilizing component and the rest is polymeric matrix

5. The thermochromic composition as defined in claim 3, in which said composition contains at least one functional additive, e.g. dye, pigment, UV absorber, antioxidant, reduction preventing agent, reducing agent, flame retardant, chelating agent etc.

6. The thermochromic composition as defined in claim 5, in which the amount of said functional additive is at least 0.1 % by weight.

7. The thermochromic composition as defined in claim 4, in which said polymeric matrix is selected from the group comprising polycarbonates, polystyrenes, polyolefins, polyacrylates such as polymethylmethacrylates, polyvinyl derivatives, polyesther derivatives, polyvinyl chloride; cellulose derivatives such as cellulose acetate, polyurethanes, polyethylene terephthalate; silicone resins such as LSR (liquid silicone rubber), triethylene glycole dimethacrylate (TEGDM, commercially known as CR-39), epoxy resins.

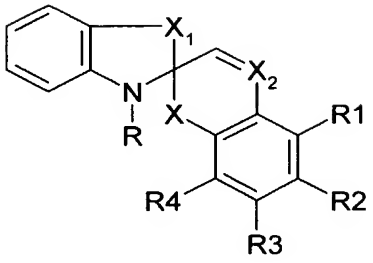


Fig. 1, Formula A

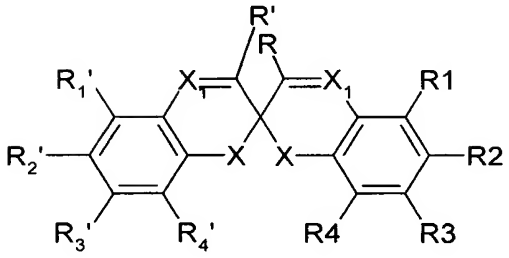


Fig.2, Formula B

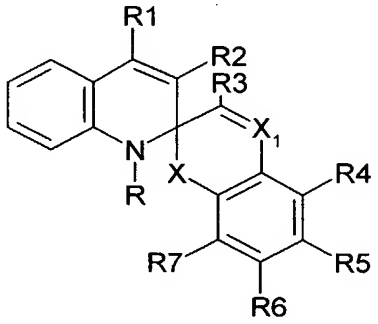
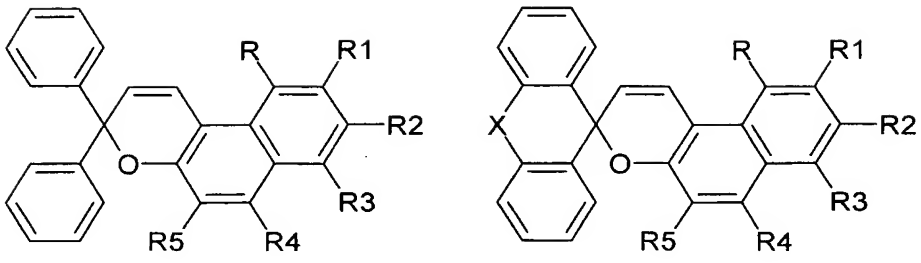


Fig.3, Formula C



D E

Fig.4, Formulae D,E

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL01/00552

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :G02F 1/00; G02B 5/23

US CL :252/583, 586

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/583, 586

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,084,702 A (BYKER et al) 04 July 2000, see column 12, lines 24 - 63 and the claims.	1 and 3-7
X --- Y	US 5,919,404 A (FUJITA et al) 06 July 1999, see column 11, line 40 - column 12, line 53.	1, 3 --- 4-7
X ---- Y	US 5,558,700 A (SHIBAHASHI et al) 24 September 1996, see claims 1 and 2.	1, 3 --- 4-7
X --- Y	US 5,480,482 A (NOVINSON) 02 January 1996, see claims 1-4 and column 7, lines 19-24.	1, 3 --- 4-7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 27 NOVEMBER 2001	Date of mailing of the international search report 14 DEC 2001
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer PHILIP C. TUCKER Telephone No. (703) 308-0651

Form PCT/ISA/210 (second sheet) (July 1998)★